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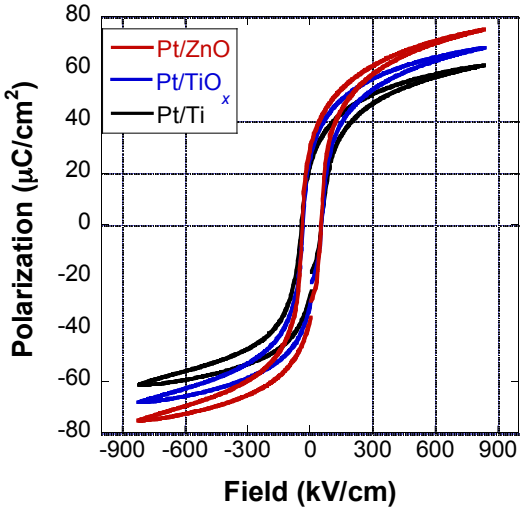

Solution Chemistry, Substrate, and Processing Effects on the Chemical Heterogeneity in PZT Films

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Collaborators

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Microscopy

- Paul Kotula
- Bryan Gauntt
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- Bonnie McKenzie
- Amy Allen
- Michael Rye
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Solution/Film Preparation

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- Erik Spoerke
- Mia Blea-Kirby
- Kelsey Meyer
- Harlan Brown-Shaklee

A brief history of ferroelectric thin film substrates*

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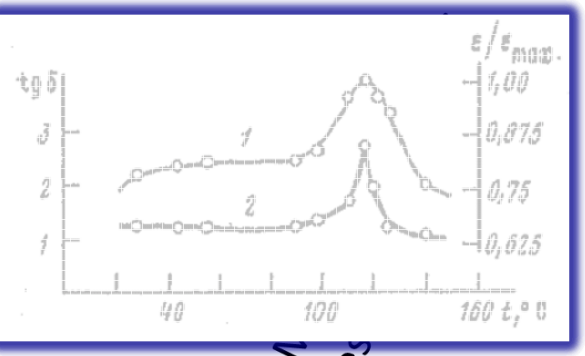
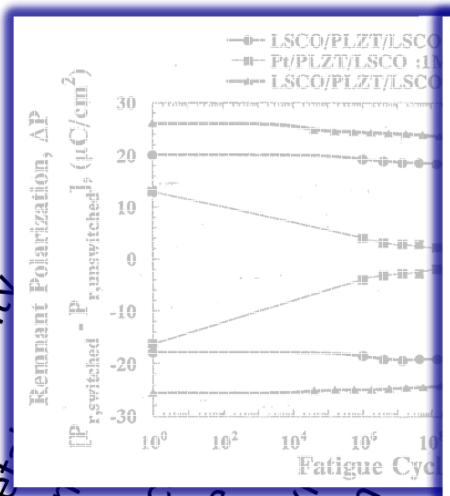
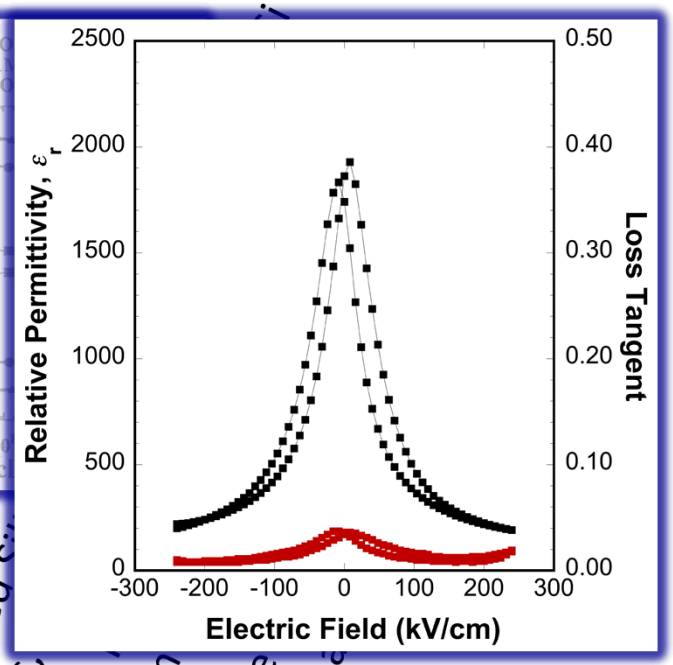






Platinum
Pratt & Fires
others

Platinized Silicon: Pt/SiO_2/Si
Virtually Entire Community

Non-Noble Met
Sayer, Newnha

Platinized Silic
Virtually Entire

Conductive Ox
Kingon and Ram

Platinized
Dimos

Base
Kingon

Base
Clem

??

Despite these substrate advances platinized silicon is by far the most utilized in R&D and piezo-MEMS settings

* Not a comprehensive history – apologies to those not included

Lessons Learned (and forgotten?)

Tani and Payne 1992

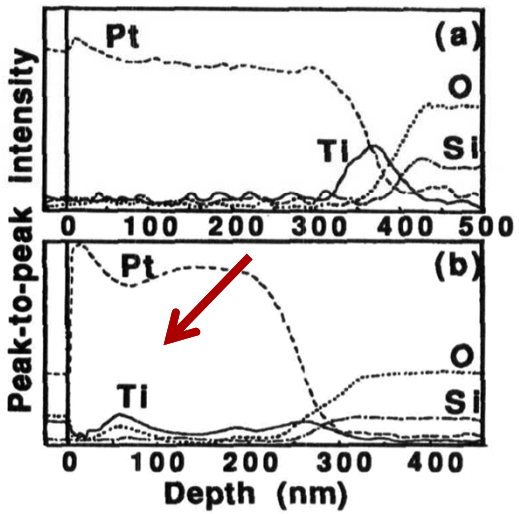
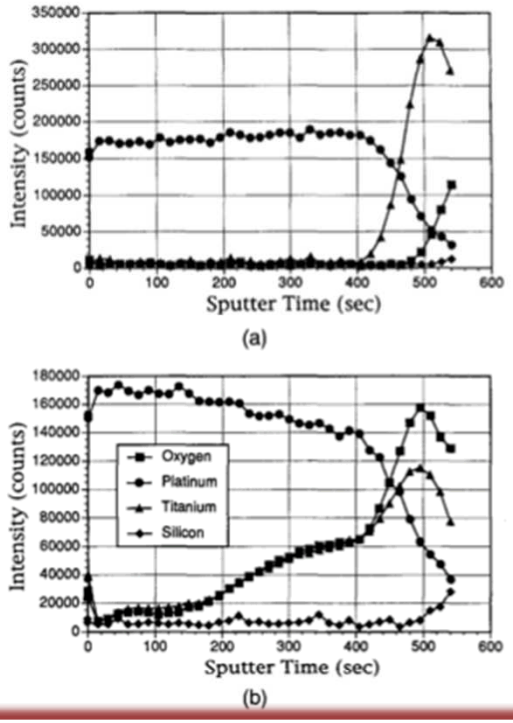


Fig.2 AES of A substrates (a) before and (b) after annealing at 650 °C for 30 min.

Fox, *et al*. 1994



Kim, *et al*. 2000

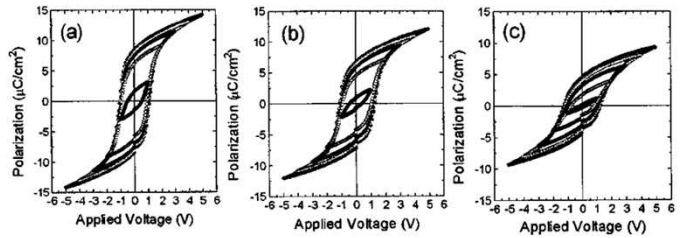
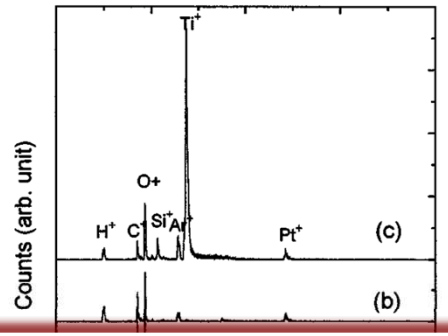
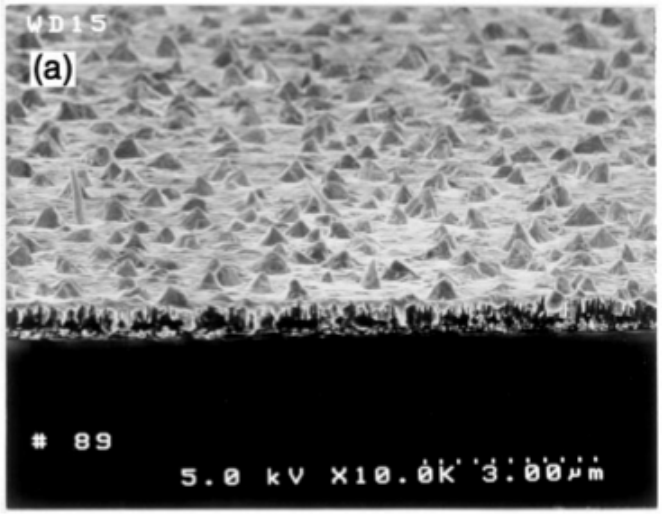


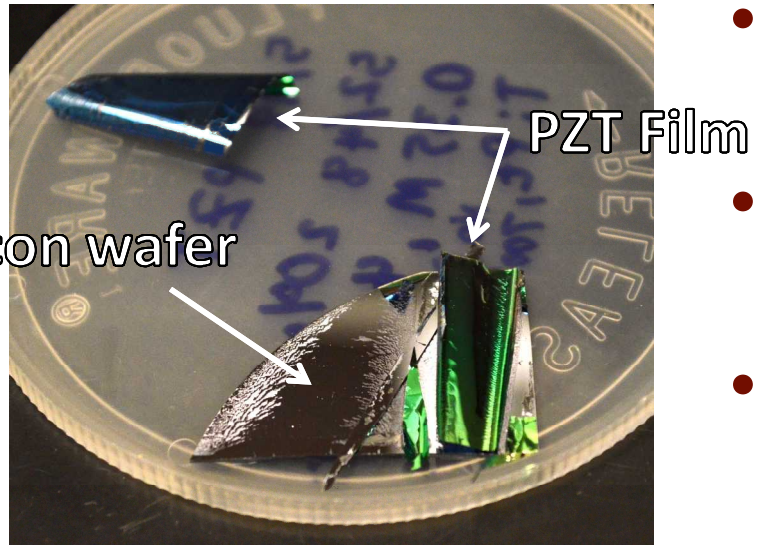
FIG. 2. $P-V$ hysteresis loops of SBT thin films (a) on $Pt/ZrO_2/SiO_2/Si$, (b) $Pt/TiO_2/SiO_2/Si$, and (c) $Pt/Ti/SiO_2/Si$ substrates.



- Electrode/adhesion layer stacks cannot be considered as inert bystanders!
- Titanium-based adhesion layers are known to diffuse through platinum

Pt/Ti remains state of the art in platinized silicon:

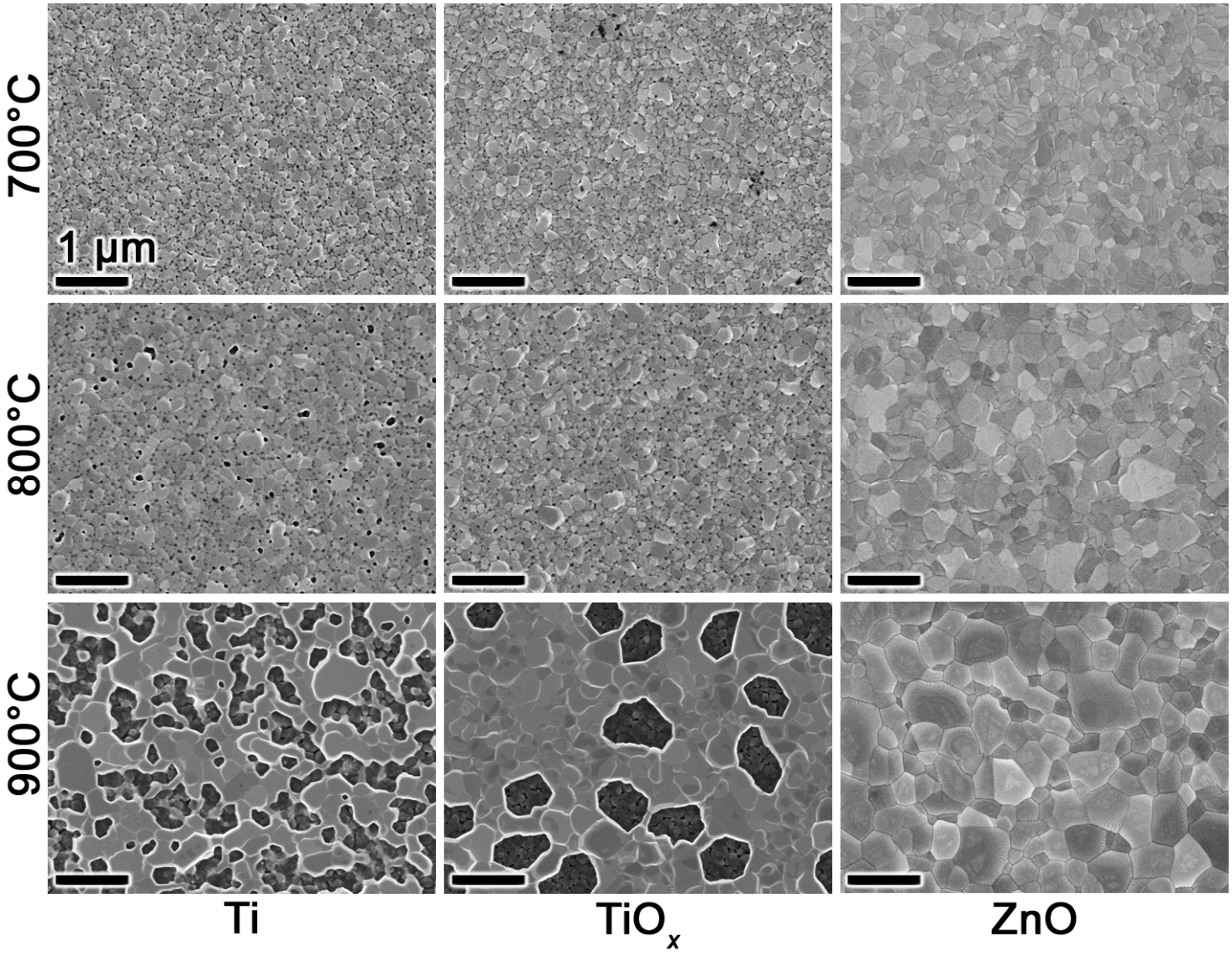




- Titanium 'adhesion' layers by far the most common
  - Adhesion of Pt/ZrO_2 and Pt/TiO_2 not as good as Pt/Ti
- Titanium expands upon oxidation causing hillocks
- Adhesion layer still fails with large temperature swings (>700°)
- ***>20 years of research and small improvements made***
- ***There must be a better solution!***
  - ***ZnO adhesion layers***

Al-Shareef, *et al.*, *J. Mat. Research*, **12** (2), 347-354 (1997)

Electrode Temperature Stability



SNL IMO PZT CSD Film Preparation

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$Zr(Obu)_4$ · BuOH + $Ti(OiPr)_4$
Blend 5 min

Acetic Acid / Methanol
Chelating agent / Solvent

$Pb(OAc)_4$ + $La(OAc)_3 \cdot H_2O$
Dissolve at ~90°C

Acetic Acid / Methanol
Adjust Molarity

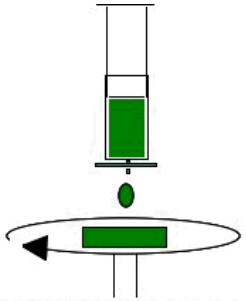
Spin Coat Deposition
4000rpm/30sec

multiple depositions

Pyrolysis

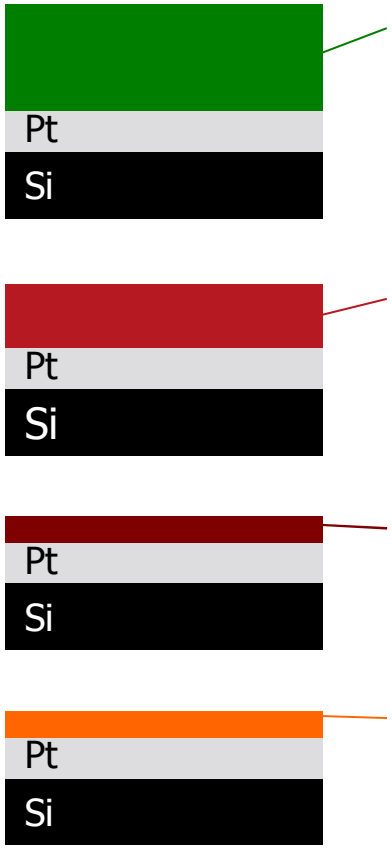
Crystallization

Sputter Pt electrodes



Spin Deposition

heating



Deposited solution

Amorphous gel ~100-300 °C

Intermediate fluorite ~400-500 °C

Perovskite ~500-700 °C

PZT Films Ferroelectric Properties: Pt/ZnO Substrates Superior

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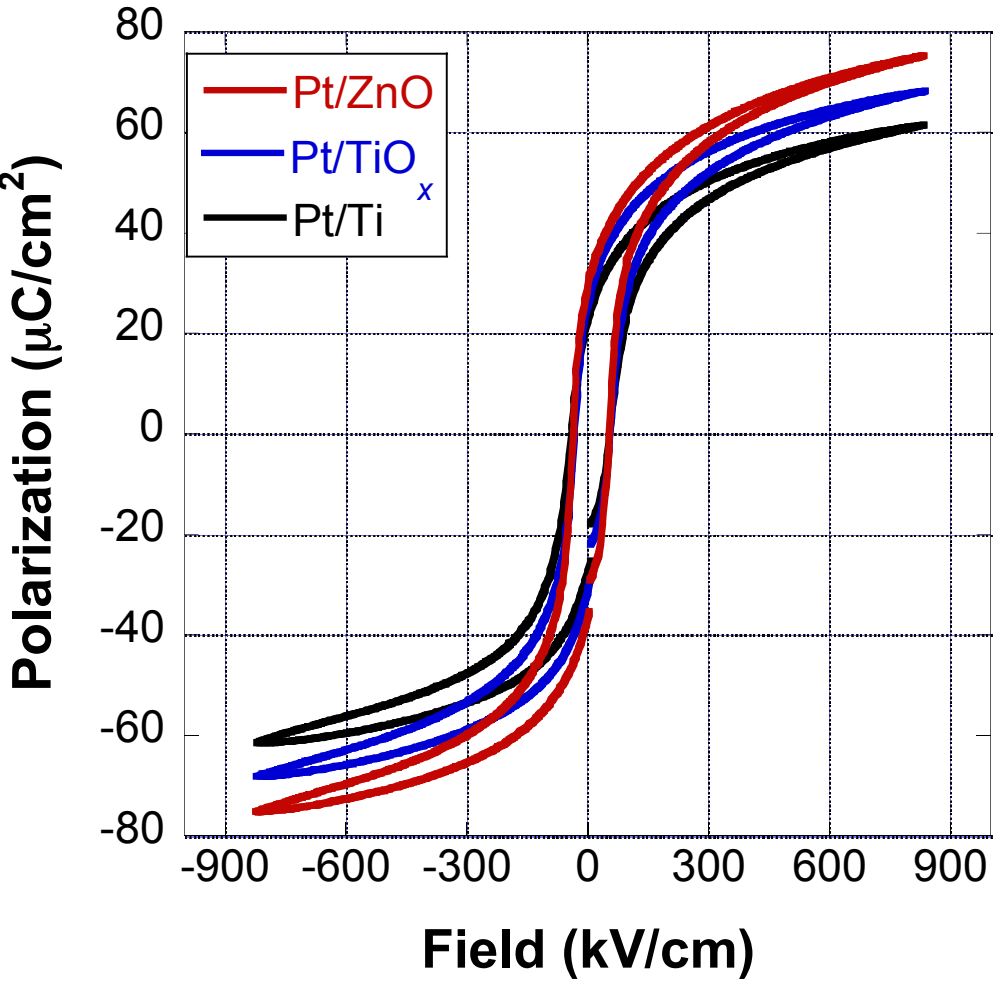
	P_{max} (μC/cm²)	P_r (μC/cm²)	E_c (kV/cm)	K
Pt/Ti	61.5	23.8	47.0	1440
Pt/TiO_x	68.2	27.0	44.1	1620
Pt/ZnO	**75.3**	**32.2**	**43.8**	**1740**

- Both P_r and K increase on ZnO-buffered substrates
- Coercive field decreases slightly for PZT on ZnO-buffered substrates



PZT Composition Analysis: No Composition Gradient on Pt/ZnO

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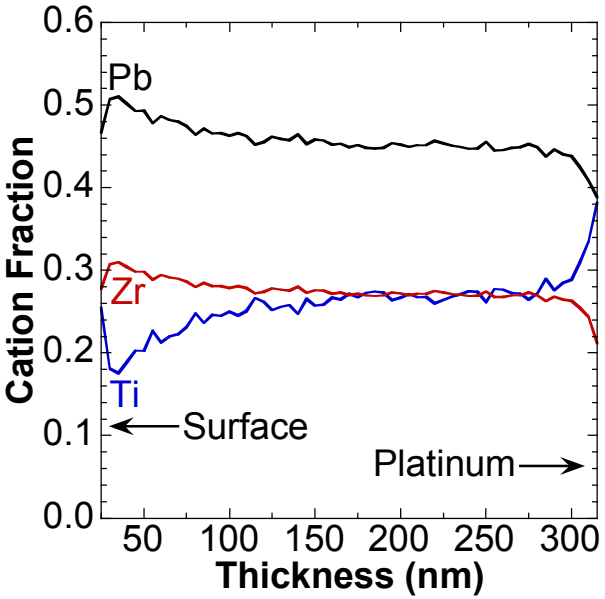
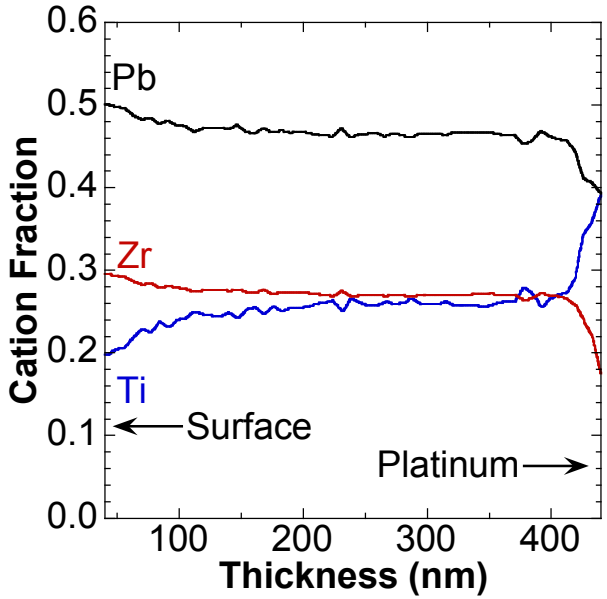
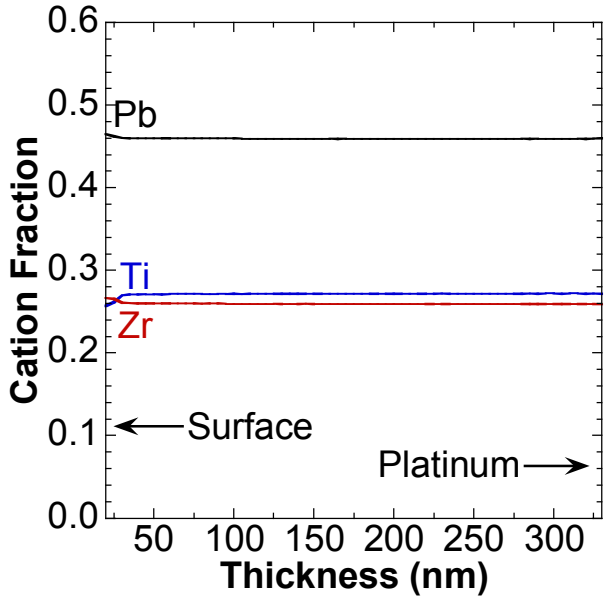
Pt/Ti



Pt/TiO$_x$

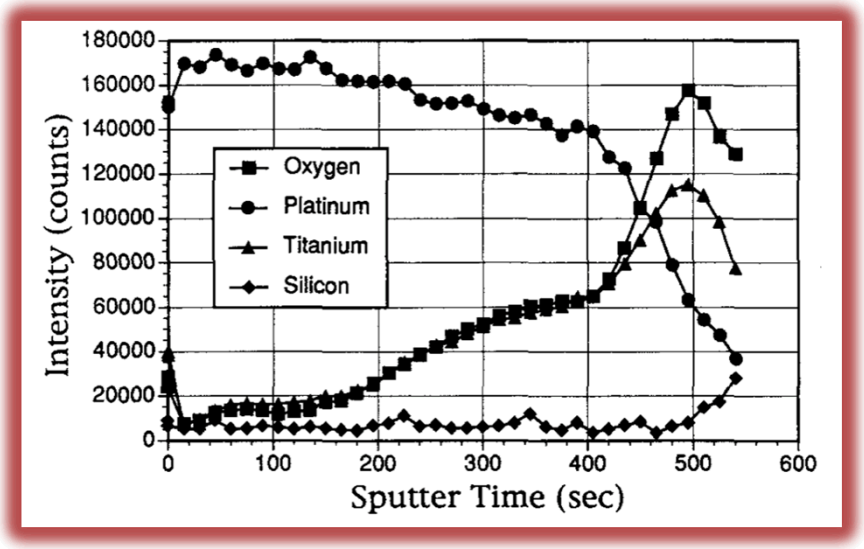


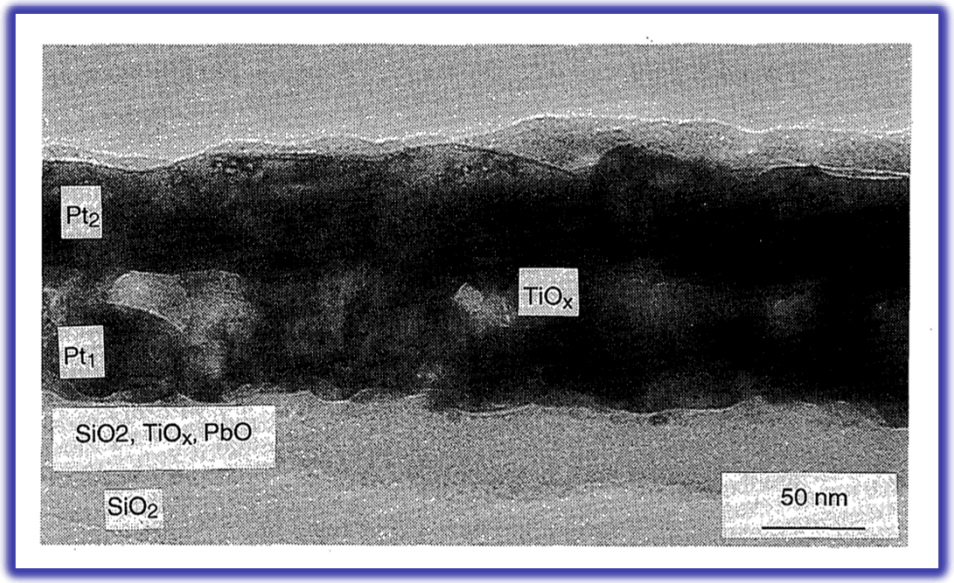
Pt/ZnO

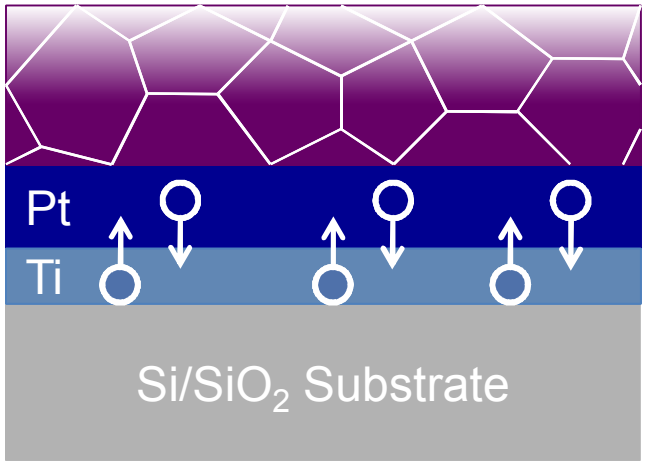


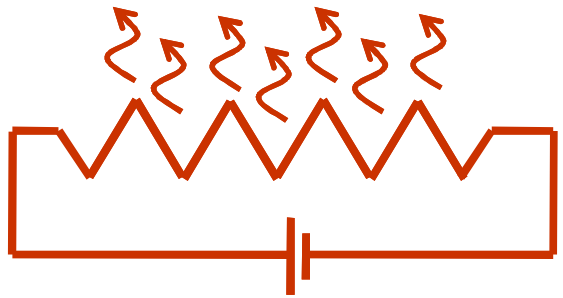
Substantially improved chemical homogeneity in films on Pt/ZnO substrates

Revising prior art: Ti diffuses into Pt!









Ti diffusing through Pt can incorporate into the PZT Film

Data from: Fox, *et al.* JACerS 1994, Maeder,*et al.* JJAP 1998

Solution Chemistry Effects?

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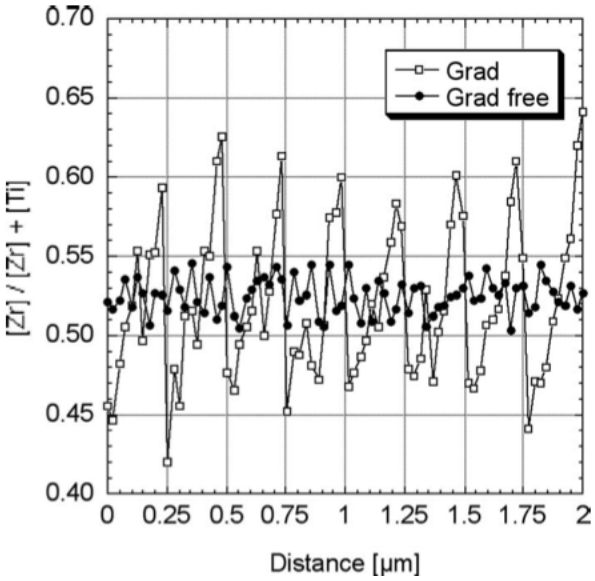
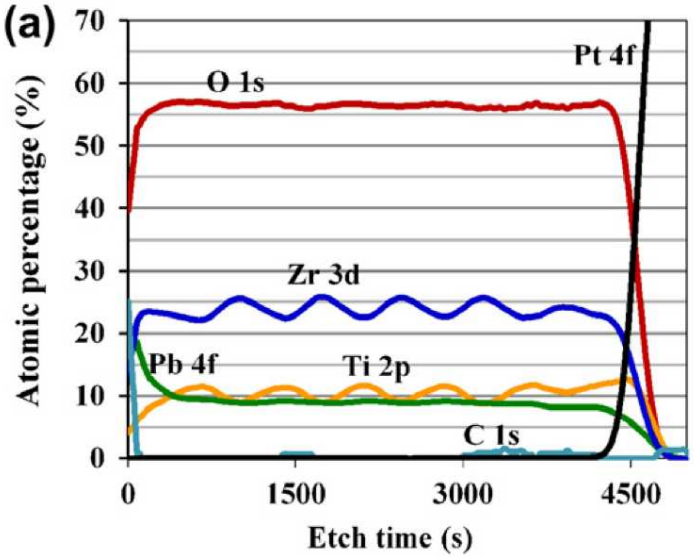
Open Issues:

- This model cannot explain 'saw-tooth' profiles observed by other groups*
- What roles do solution chemistry and processing conditions play in gradient formation?
- More experiments necessary to isolate controlling variables
  - ***Substrate: Pt/Ti vs Pt/ZnO***
  - ***Chemistry: IMO vs 2-MOE‡***
  - ***Pyrolysis: 300, 350, 400° C***
  - Heating Method/Rate: 15, 50, 200° C/s

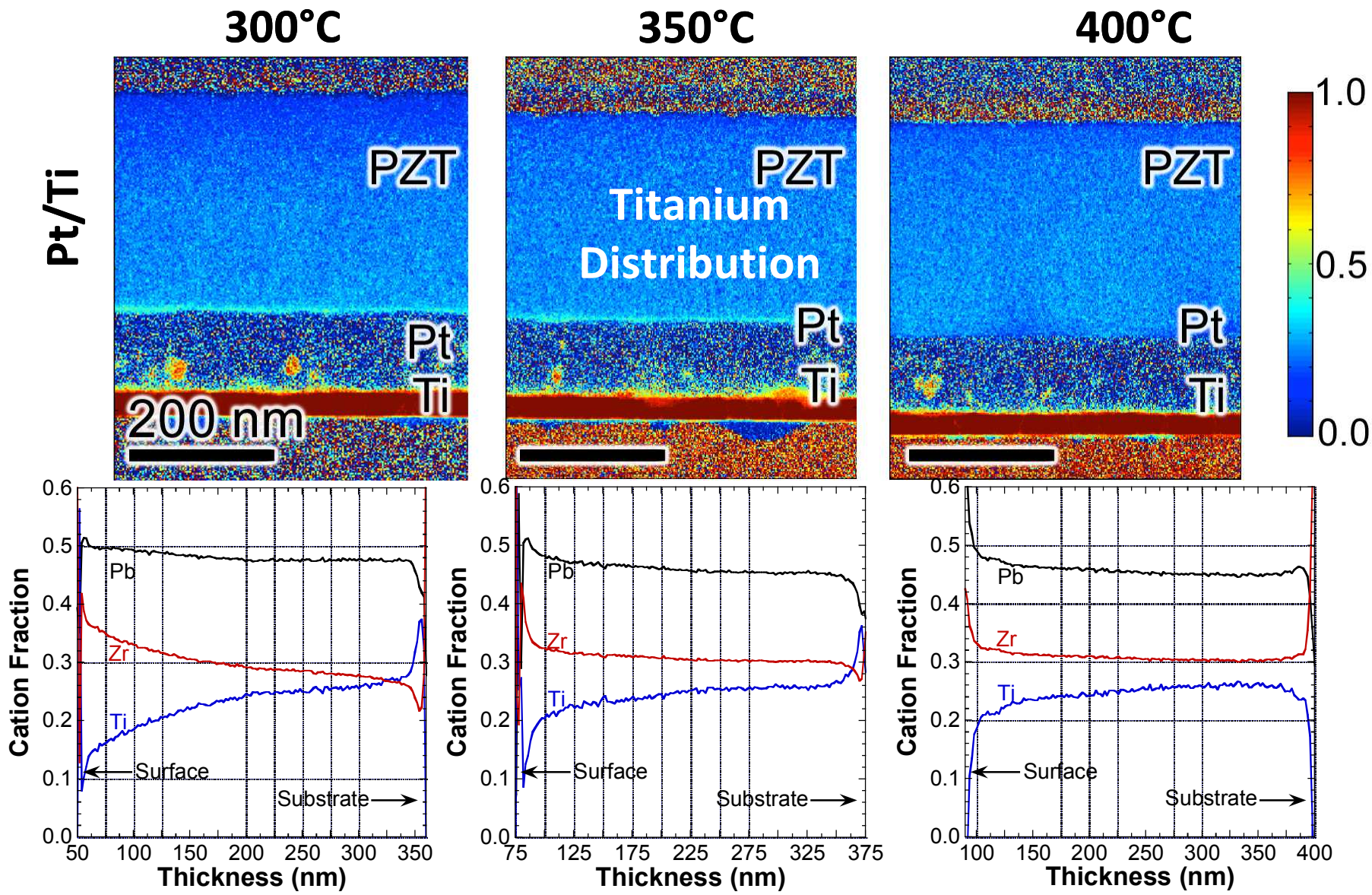




*Amanuma, *et al.*, *Appl. Phys. Lett.* **65,** 3140 (1994)
Calame and Muralt, *Appl. Phys. Lett*. **90**, 062907 (2007), Bastani and Bassiri-Gharb, *Acta. Mater*. **60**, 1346 (2012)

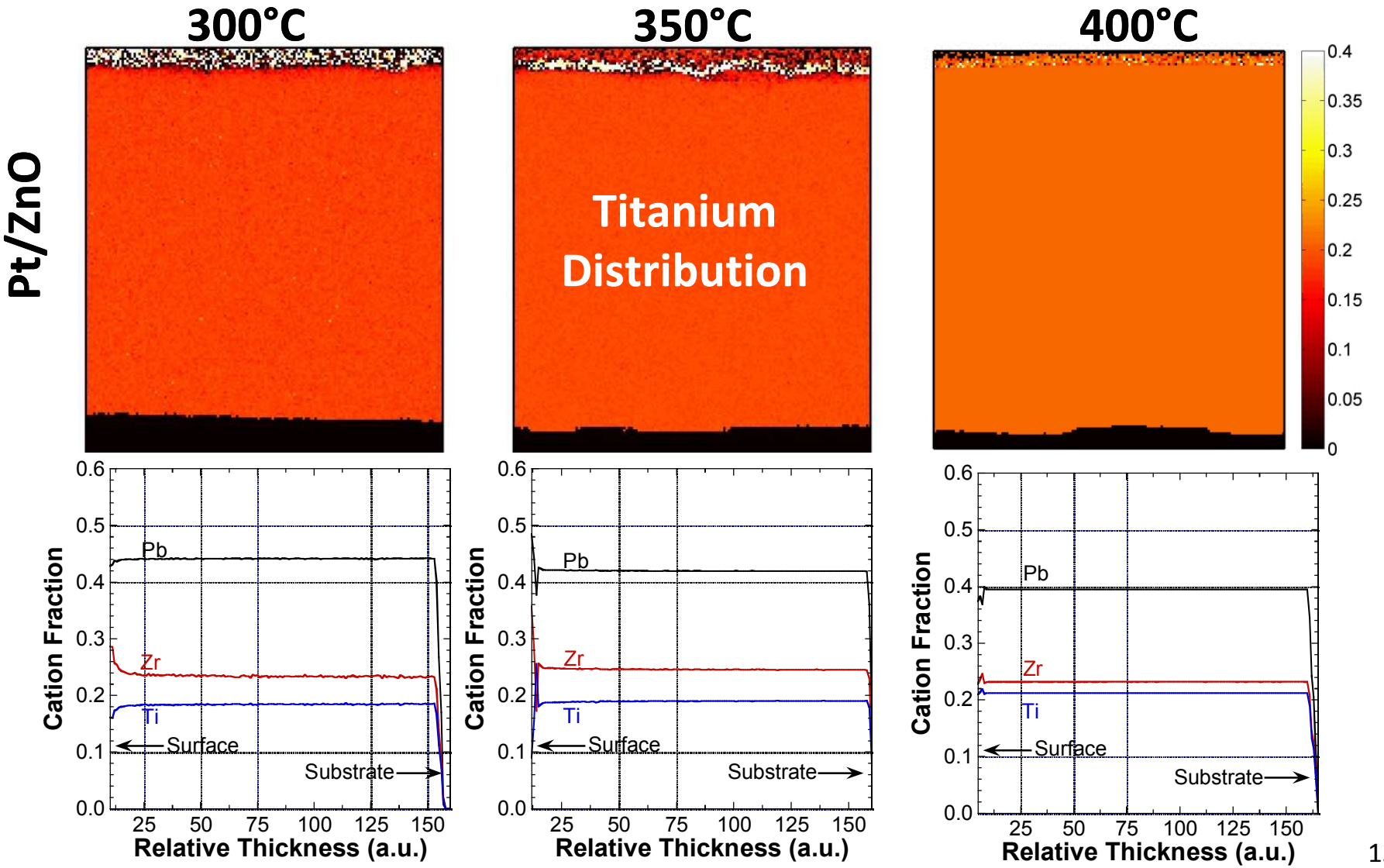
‡Based upon: C.D.E. Lakeman and D.A. Payne, JACerS, **75(11)**, 3091 (1992)

Solution Chemistry Effect: IMO films



Solution Chemistry Effect: IMO Films

Sandia National Laboratories



Solution Chemistry Effect: 2-MOE films

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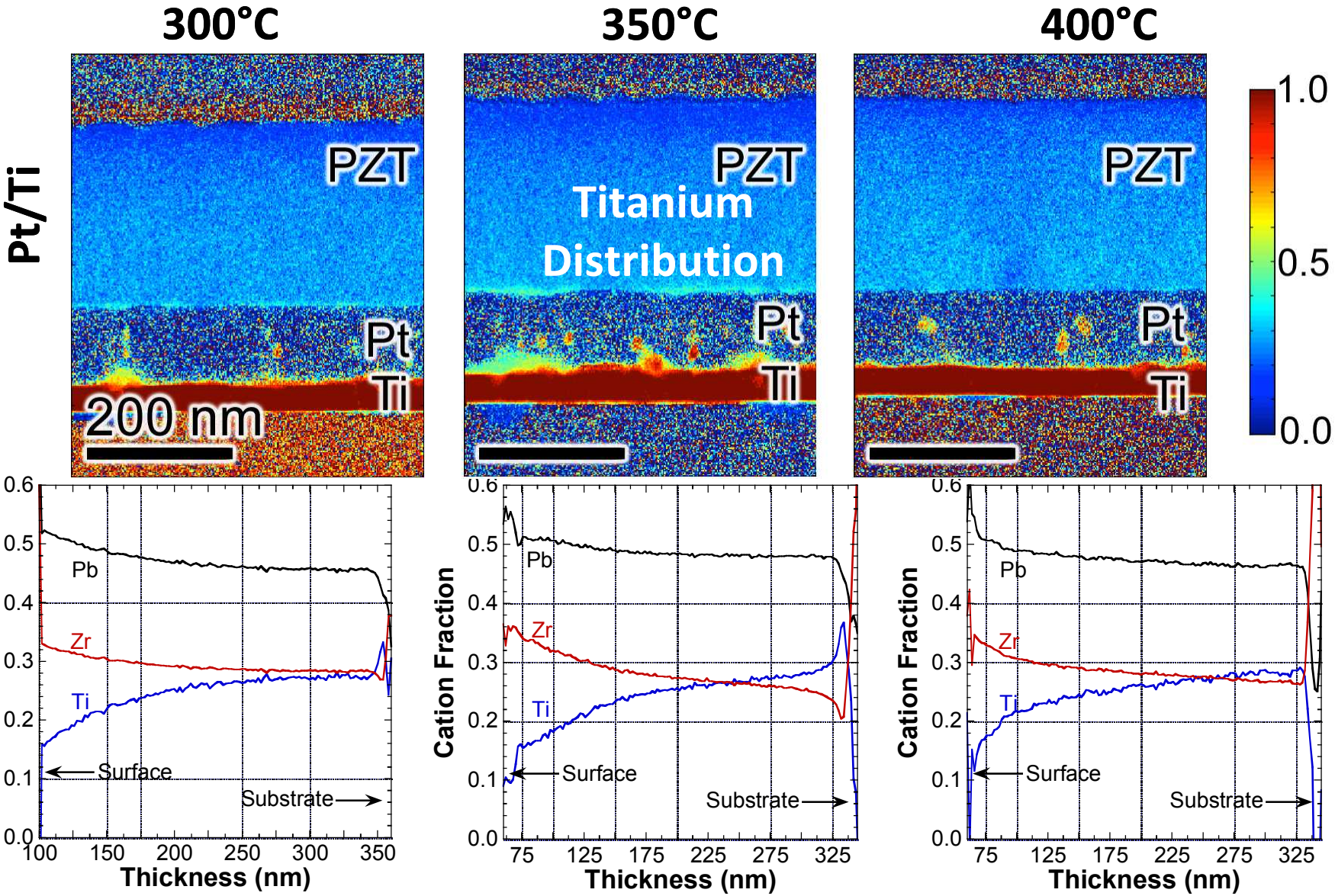
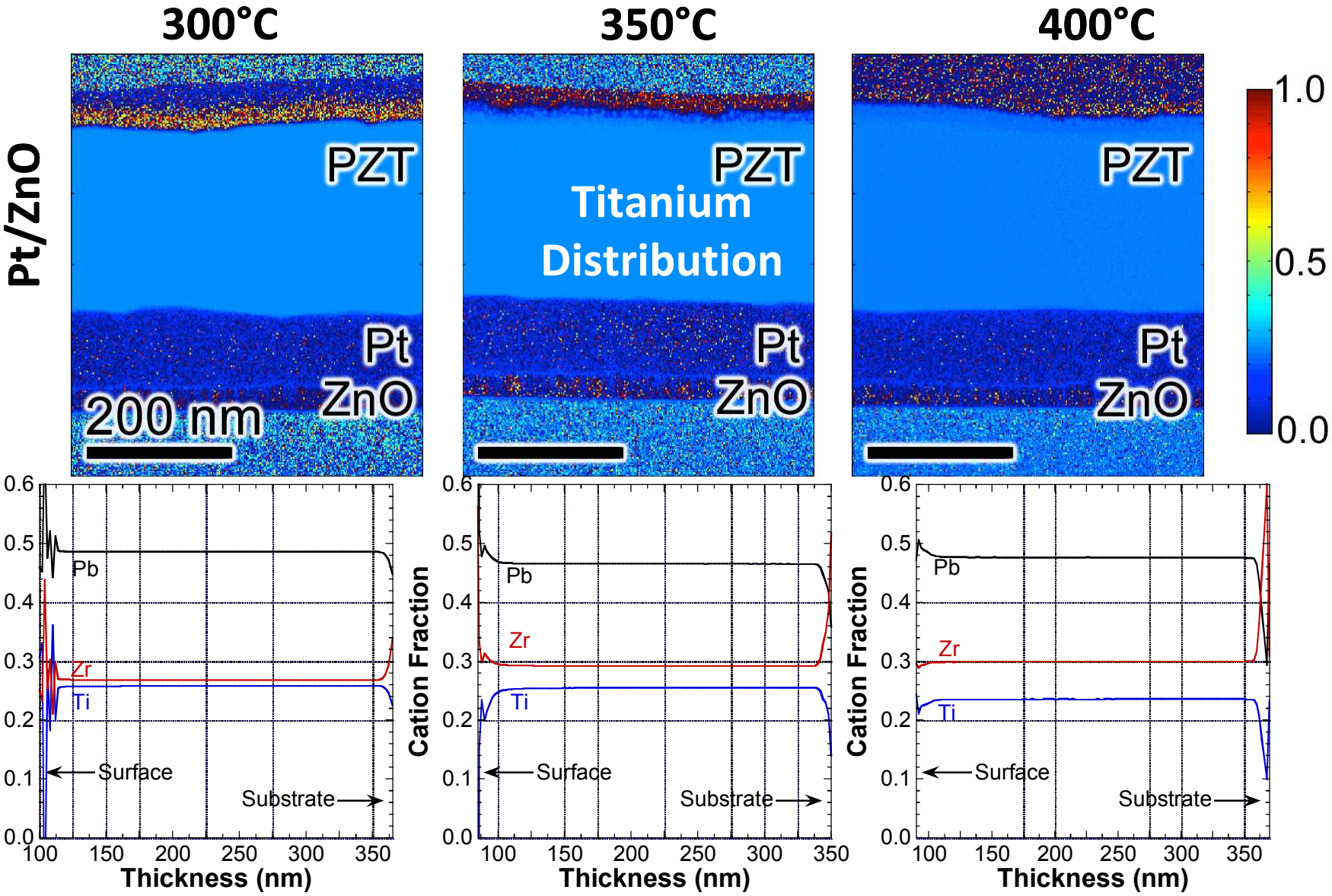


Solution Chemistry Effect: 2-MOE films

Sandia National Laboratories



Solution Chemistry Effects?

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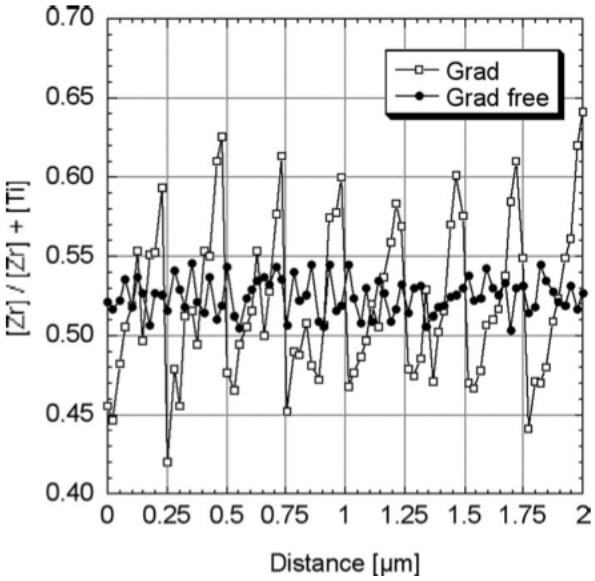
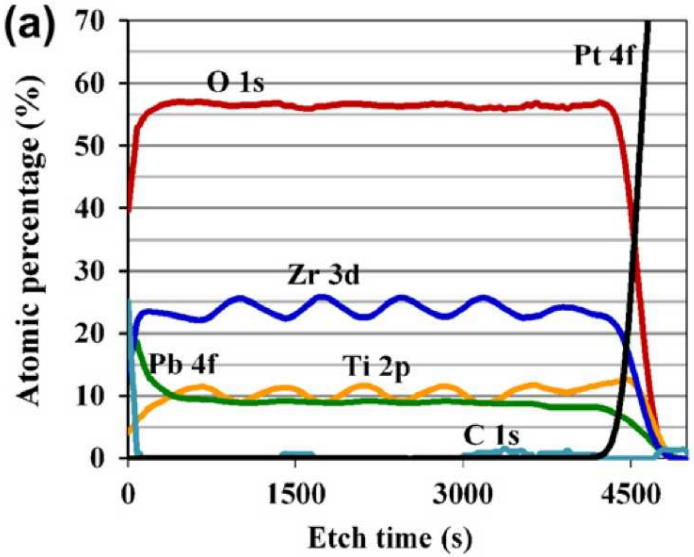
Open Issues:

- This model cannot explain 'saw-tooth' profiles observed by other groups*
- What roles do solution chemistry and processing conditions play in gradient formation?
- More experiments necessary to isolate controlling variables
  - ~~Substrate: Pt/Ti vs Pt/ZnO~~
  - ~~Chemistry: IMO vs 2-MOE‡~~
  - ~~Pyrolysis: 300, 350, 400° C~~
  - ***Heating Method/Rate: 15, 50, 200° C/s via RTA***





*Amanuma, *et al.*, *Appl. Phys. Lett.* **65,** 3140 (1994)
Calame and Muralt, *Appl. Phys. Lett*. **90**, 062907 (2007), Bastani and Bassiri-Gharb, *Acta. Mater*. **60**, 1346 (2012)

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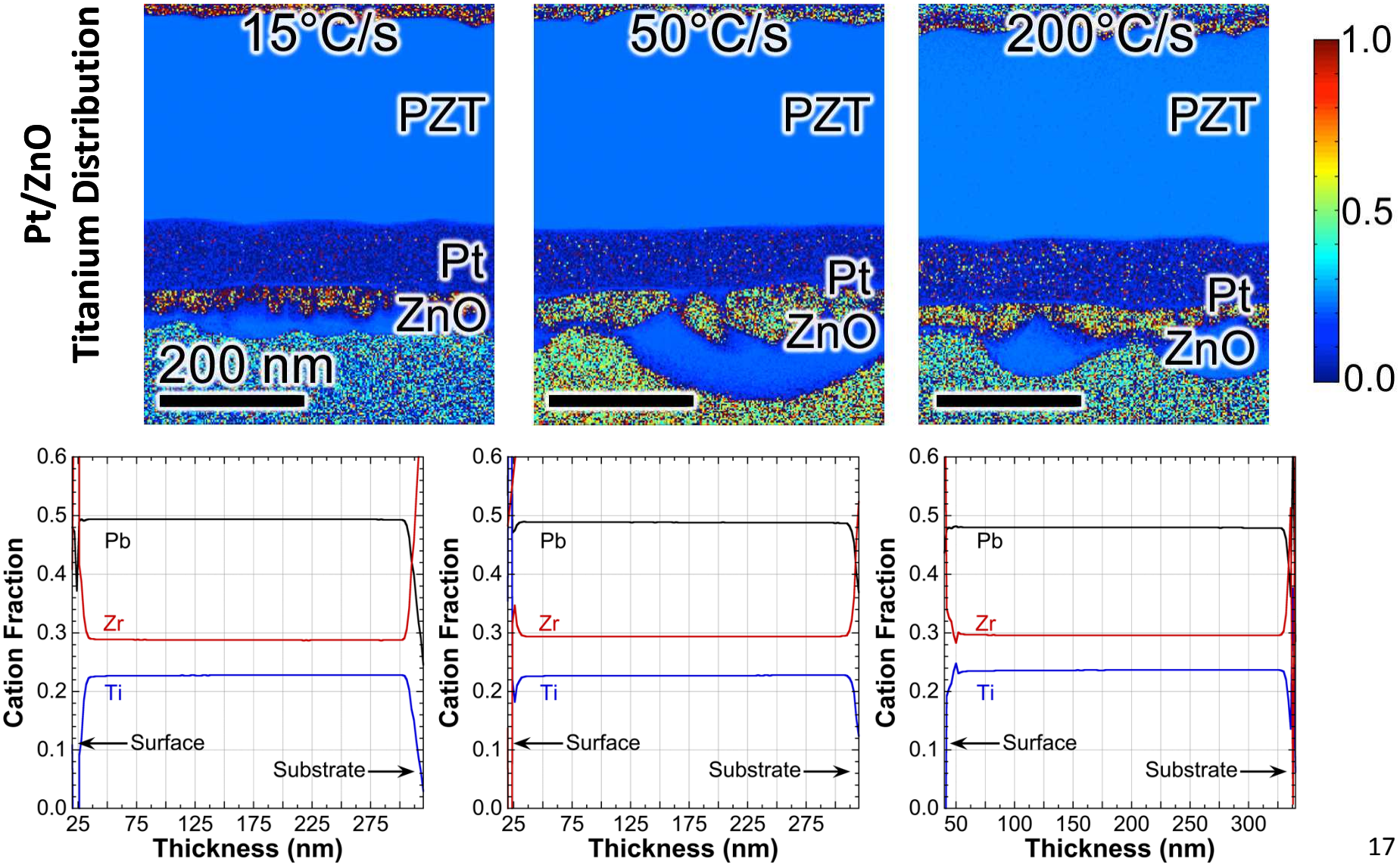
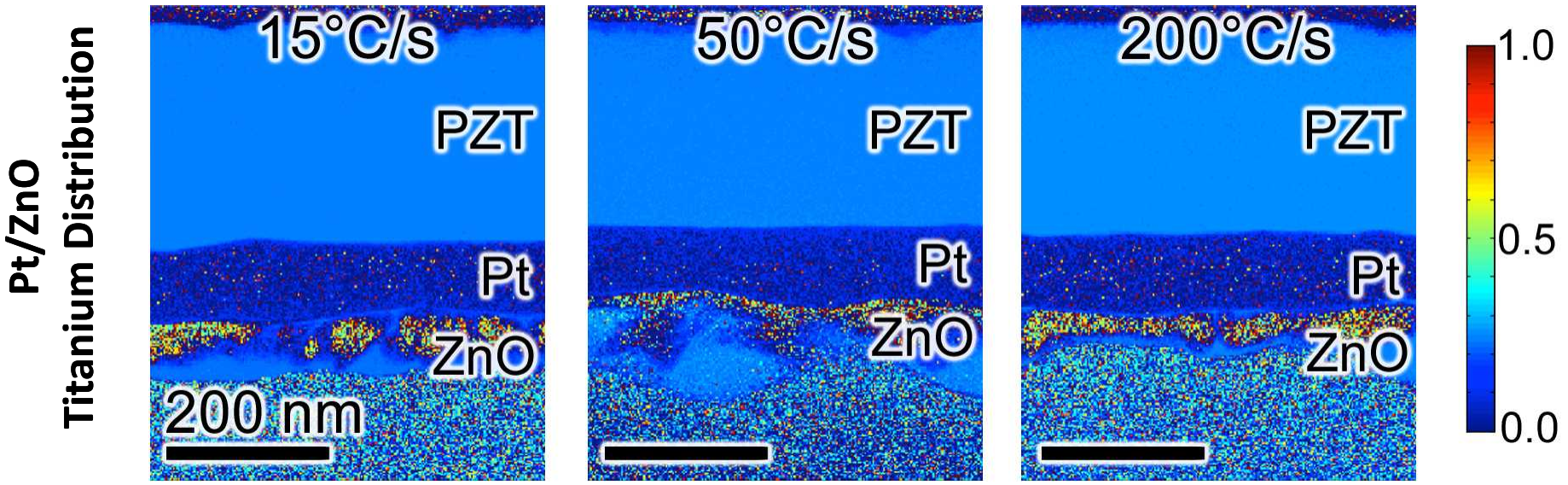
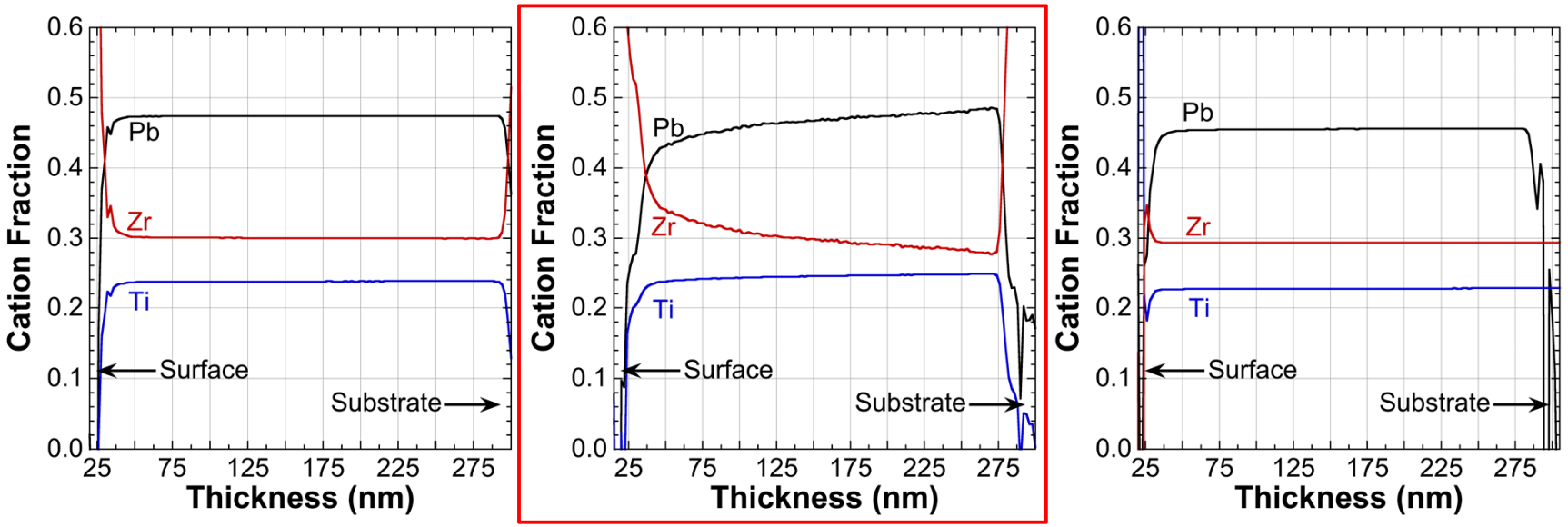
Ramp Rate Effect: IMO Films

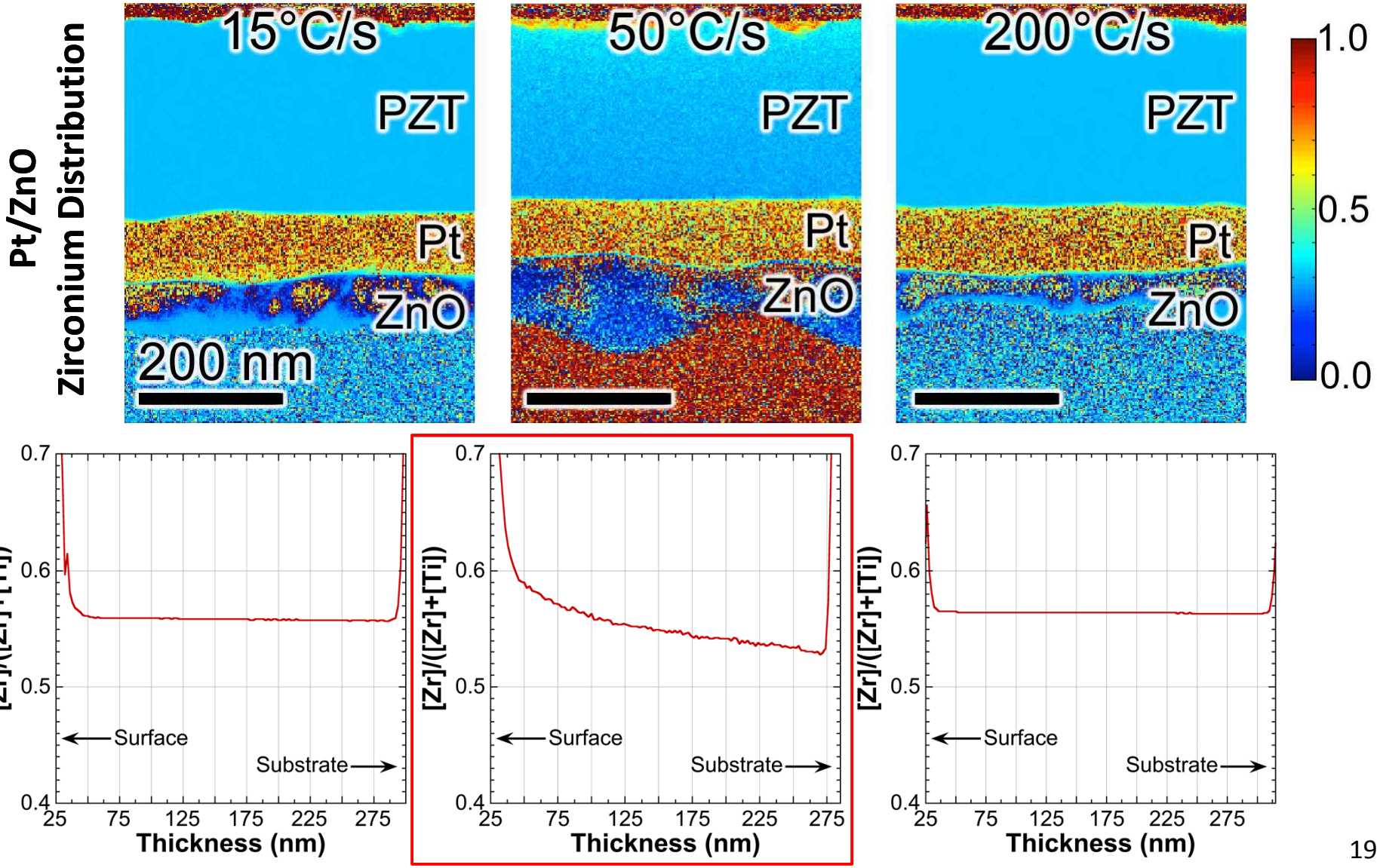


Ramp Rate Effect: 2-MOE Films



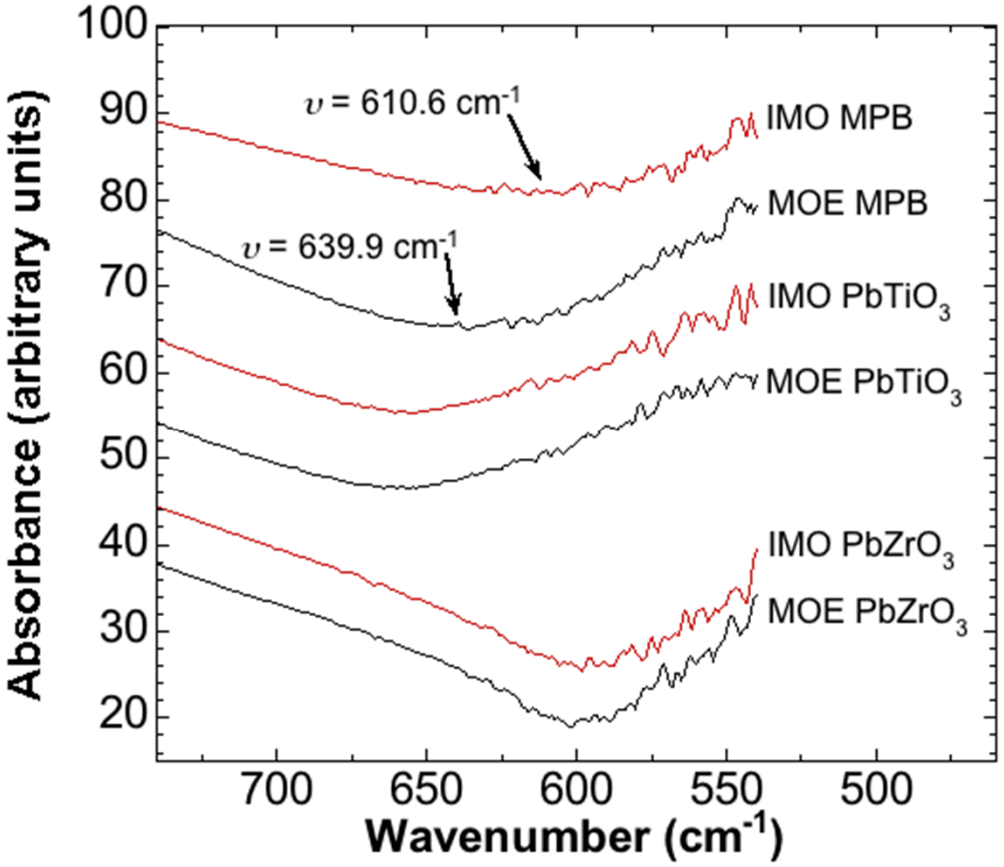


Ramp Rate Effect: 2-MOE Films



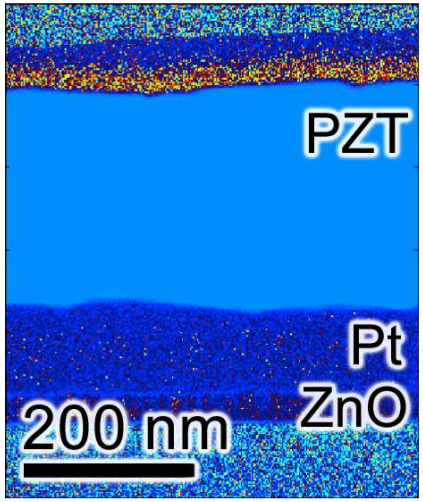
Possible Explanation: IR properties

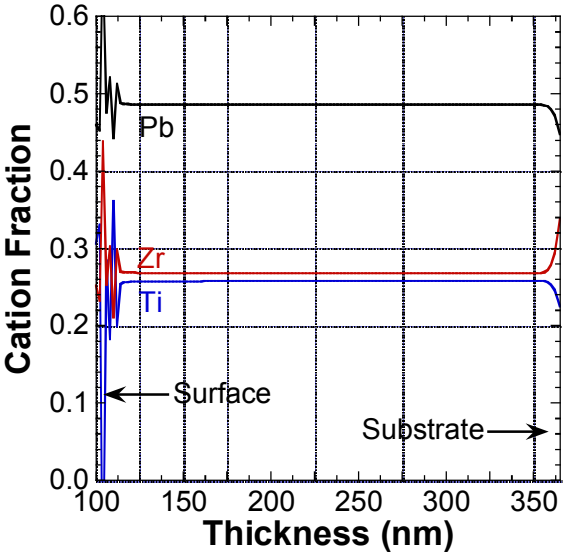
- Heating mechanism differs
  - RTA=Optical absorption
  - Furnace=optical+conductive
- IR spectra of pyrolyzed gels differs for IMO and 2-MOE chemistries
  - 2-MOE "*looks*" like $PbTiO_3$
  - IMO "*looks*" like $PbZrO_3$
- $PbTiO_3$ absorption closer to IR irradiance peak from RTA
  - Potential preferential absorption

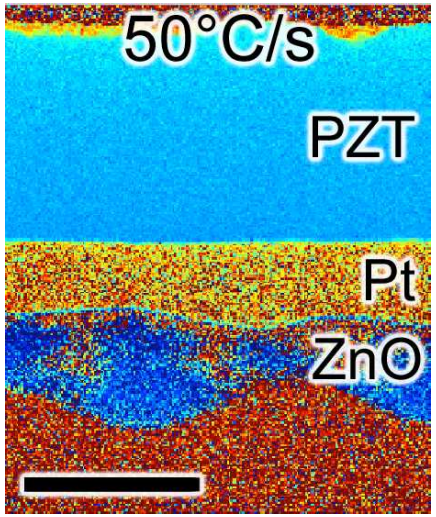


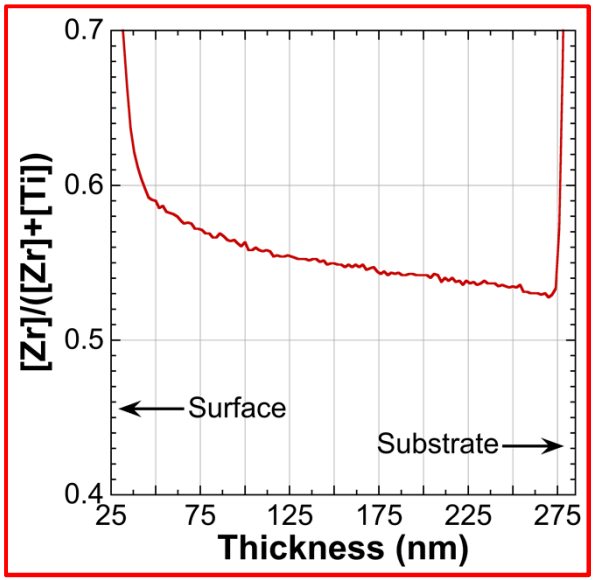
Processing of PZT Film: Lessons Learned To Date

- Pyrolysis temperature does not significantly effect gradient formation
- For furnace anneals gradient formation appears to be hindered – even for 2MOE sol-gel chemistries
- *Heating rate, method, and solution chemistry **does** appear to matter*
  - Slight gradient observed in RTA samples with 50° C/s ramp rate









Summary

- IMO PZT films prepared on Pt/ZnO substrates possess improved electronic properties compared to traditional substrates
- ZnO as an adhesion layer enables chemically homogeneous films for most processing conditions
- Titanium/TiO_x may be poor choices for Pt adhesion layers for the high performance device development
- ***If a chemically homogeneous film is required, then furnace anneals are preferable***